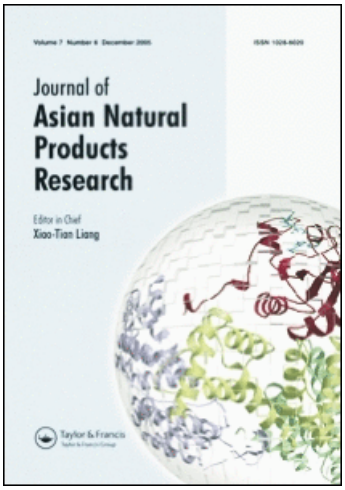


Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Tenuifoliose Q, a new oligosaccharide ester from the root of *Polygala tenuifolia* willd.

Yong Jiang; Peng-Fei Tu

Online publication date: 12 May 2010

To cite this Article Jiang, Yong and Tu, Peng-Fei(2003) 'Tenuifoliose Q, a new oligosaccharide ester from the root of *Polygala tenuifolia* willd.', Journal of Asian Natural Products Research, 5: 4, 279 — 283
To link to this Article: DOI: 10.1080/1028602031000111987
URL: http://dx.doi.org/10.1080/1028602031000111987

Journal of Asian Natural Products Research, 2003 VOL. 5 (4), pp. 279–283

TENUIFOLIOSE Q, A NEW OLIGOSACCHARIDE ESTER FROM THE ROOT OF *POLYGALA TENUIFOLIA* WILLD.

YONG JIANG and PENG-FEI TU*

Modern Research Center of TCM, School of Pharmaceutical Sciences, Peking University Health Science Center, Beijing 100083, China

(Received 23 December 2002; Revised 23 January 2003; In final form 7 March 2003)

From the cortexes of *Polygala tenuifolia* Willd., a new oligosaccharide ester, tenuifoliose Q (**1**), was isolated together with three known compounds. The structure of **1** was elucidated by spectroscopic and physiochemical analysis as an oligosaccharide esterified with acetic, benzoic and *p*-hydroxycinnamoyl acid.

Keywords: *Polygala tenuifolia*; Oligosaccharide ester; Tenuifoliose Q

INTRODUCTION

It has been reported that plenty of oligosaccharide esters have been isolated from the genus of *Polygala* [1–4]. The rarity of structures of this type of constituents inspired us to investigate further for additional oligosaccharide esters from the root of *Polygala tenuifolia* Willd., a well-known traditional Chinese medicine used as an expectorant, tonic, sedative and for preventing dementia [5]. We have already isolated four compounds with this skeleton, and one of which was a new one. Here, we report the isolation and structure elucidation of the new oligosaccharide ester tenuifoliose Q from the cortexes of *Polygala tenuifolia*, together with three known homologous compounds (Fig. 1).

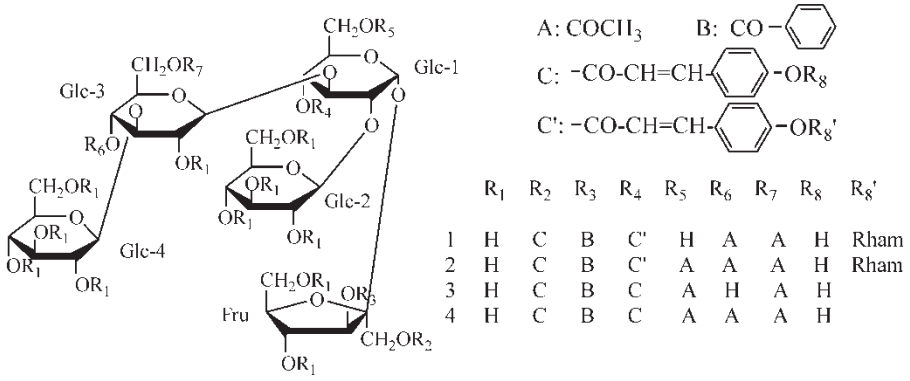
RESULTS AND DISCUSSION

The n-BuOH-soluble parts of the 95% EtOH extract of *P. tenuifolia* were subjected to macroporous resin D101 column chromatography, eluted with gradient EtOH—H_2O. The 50% aq. EtOH eluate was chromatographed on silica gel, ODS column and by HPLC to afford tenuifoliose Q, along with three known oligosaccharide esters.

Tenuifoliose Q (**1**) was obtained as a white amorphous powder and its molecular formula deduced to be $C_{65}H_{82}O_{37}$ from its TOF-MS (1477 $[M + Na]^+$) and by ^{13}C NMR analysis.

*Corresponding author. Tel.: +86-10-62092750. Fax: +86-10-62092750. E-mail: pengfeitu@mail.bjmu.edu.cn

ISSN 1028-6020 print/ISSN 1477-2213 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/1028602031000111987



	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_8'
1	H	C	B	C'	H	A	A	H	Rham
2	H	C	B	C'	A	A	A	H	Rham
3	H	C	B	C	A	H	A	H	
4	H	C	B	C	A	A	A	H	

FIGURE 1 Structures of compounds **1**–**4**.

The IR spectrum of **1** showed the presence of hydroxyl groups (3405 cm^{-1}), carbonyl group (1720 cm^{-1}), double bond (1633 cm^{-1}), and aromatic rings (1604, 1513, 1452 cm^{-1}). The ^{1}H NMR spectrum of **1** (see Table I) showed a group of benzoyl proton signals at δ 8.21 (2H, dd, J = 8.0, 1.5 Hz), 7.60 (2H, t, J = 8.0 Hz) and 7.70 (1H, tt, J = 8.0, 1.0 Hz); two groups of *p*-hydroxycinnamoyl proton signals at δ 7.37 (2H, d, J = 8.0 Hz), 6.79 (2H, d, J = 8.5 Hz), 6.33 (1H, d, J = 16.0 Hz), 7.64 (1H, d, J = 16.5 Hz), 7.13 (2H, d, J = 8.5 Hz), 7.54 (2H, d, J = 8.5 Hz), 6.32 (1H, d, J = 15.5 Hz) and 7.60 (1H, d, J = 15.5 Hz), together with two acetyl proton signals at δ 1.98 and 1.51 (3H each, s). In addition, in the ^{1}H NMR spectrum of **1**, there are five anomeric proton signals at δ 5.86 (1H, d, J = 3.0 Hz), 4.57 (1H, d, J = 7.5 Hz), 4.50 (1H, d, J = 8.0 Hz) 4.45 (1H, d, J = 7.5 Hz), 5.53 (1H, brs) and a H-3 proton signal of fructose at δ 5.71 (1H, d, J = 8.5 Hz). All these data suggested that **1** is an oligosaccharide esterified with acetic, benzoic and *p*-hydroxycinnamoyl acids. On acid hydrolysis, **1** gave glucose and fructose. The NMR data of **1** are very similar to those of tenuifoliose L [1], except that an acetyl signals at δ 2.06 of tenuifoliose L disappeared in **1**, and the C-6 signal of Glc-1 in **1** shifted 1.7 ppm upfield, while the C-5 signal shifted 3.3 ppm downfield. Therefore, we deduced that the C-6 position of Glc-1 in **1** was perhaps deacetylated. All proton signals were assigned through the TOCSY experiment, and we found that the H-6 signals of Glc-1 in **1** at δ 3.57 (1H, dd, J = 11.5, 5.0 Hz) and δ 3.69 (1H, dd, J = 11.5, 2.0 Hz) shifted 0.58 and 0.51 ppm upfield, compared with those signals in tenuifoliose L. Moreover, all the proton signals of Glc-1 in **1** were the same as those of tenuifoliose J [1], which does not have an acetyl group at H-6 of Glc-1. Thus, the structure of **1** was concluded to be that shown in Fig. 1.

Compounds **2**–**4** were identified by comparing their physical and spectral data (Table II) with the literature values, as tenuifoliose L (**2**), tenuifoliose I (**3**) and tenuifoliose H (**4**) [1].

EXPERIMENTAL

General Experimental Procedures

Optical rotations were measured on a Polartronic D polarimeter. UV spectra were recorded on a TU-1901 spectrophotometer, whereas IR spectra were obtained on an AVATER-360 spectrophotometer. MDLDI-TOF MS spectra were performed with a LDI 1700 spectrometer, using CCA (α-cyano-4-hydroxycinnamic acid) as matrix, while ESI MS spectra were performed on a QSTAR mass spectrometer. ^{1}H, ^{13}C NMR, TOCSY, HMQC and HMBC spectra were measured on a Bruker AM-500 spectrometer. D101 resin was from Tianjin

TABLE I ^{1}H NMR data of compounds **1**–**4** (500 MHz)[a]

	1	*2*	*3*	*4*
Glc-1				
1	5.86 (1H, d, $J = 3.0$ Hz)	5.89 (1H, d, $J = 3.5$ Hz)	6.62 (1H, brs)	6.62 (1H, d, $J = 3.5$ Hz)
Glc-2				
1	4.57 (1H, d, $J = 7.5$ Hz)	4.58 (1H, d, $J = 7.5$ Hz)	5.15 (1H, d, $J = 7.0$ Hz)	5.10 (1H, d, $J = 8.0$ Hz)
Glc-3				
1	4.50 (1H, d, $J = 8.0$ Hz)	4.52 (1H, d, $J = 8.0$ Hz)	5.26 (1H, d, $J = 8.0$ Hz)	5.23 (1H, d, $J = 8.0$ Hz)
Glc-4				
1	4.45 (1H, d, $J = 7.5$ Hz)	4.45 (1H, d, $J = 8.0$ Hz)	5.08 (1H, d, $J = 7.5$ Hz)	5.09 (1H,d, $J = 7.5$ Hz)
Fru				
1	4.26 (1H, d, $J = 12.0$ Hz)	4.27 (1H, d, $J = 12.0$ Hz)	4.81 (1H, d, $J = 10.5$ Hz)	4.85 (1H, d, $J = 12.0$ Hz)
	4.63 (1H, d, $J = 12.0$ Hz)	4.60 (1H, d, $J = 12.0$ Hz)	5.41 (1H, d, $J = 12.0$ Hz)	5.39 (1H, d, $J = 12.0$ Hz)
3	5.71 (1H, d, $J = 8.5$ Hz)	5.72 (1H, d, $J = 8.0$ Hz)	6.53 (1H, d, $J = 8.0$ Hz)	6.53 (1H, d, $J = 8.0$ Hz)
Rham				
1	5.53 (1H, brs)	5.53 (1H, d, $J = 1.5$ Hz)		
6	1.23 (3H, d, $J = 6.0$ Hz)	1.22 (3H, d, $J = 6.0$ Hz)		
Ac(R_5)		2.06 (3H, s)	2.14 (3H, s)	2.15 (3H, s)
Ac(R_6)	1.98 (3H, s)	1.98 (3H, s)		2.19 (3H, s)
Ac(R_7)	1.51 (3H, s)	1.51 (3H, s)	1.63 (3H, s)	1.76 (3H, s)
Bz (R_3)				
2,6	8.21 (2H, dd, $J = 8.0,\ 1.5$ Hz)	8.19 (2H, dd, $J = 8.0,\ 1.5$ Hz)	8.35 (2H, d, $J = 6.5$ Hz)	8.37 (2H, d, $J = 7.0$ Hz)
3,5	7.60 (2H, t, $J = 8.0$ Hz)	7.60 (2H, t, $J = 8.0$ Hz)	7.56 (2H, m)	7.58 (2H, d, $J = 7.0$ Hz)
4	7.70 (1H, tt, $J = 8.0, 1.0$ Hz)	7.70 (1H, tt, $J = 8.0, 1.0$ Hz)	7.58 (1H, m)	7.60 (1H, t, $J = 6.5$ Hz)
Cinn(R_2)				
2,6	7.37 (2H, d, $J = 8.0$ Hz)	7.35 (2H, d, $J = 8.5$ Hz)	7.39 (2H, d, $J = 7.5$ Hz)	7.40 (2H, d, $J = 8.5$ Hz)
3,5	6.79 (2H, d, $J = 8.5$ Hz)	6.79 (2H, d, $J = 9.0$ Hz)	7.14 (2H, d, $J = 7.5$ Hz)	7.14 (2H, d, $J = 8.0$ Hz)
β	6.33 (1H, d, $J = 16.0$ Hz)	6.31 (1H, d, $J = 16.0$ Hz)	6.66 (1H, d, $J = 16.0$ Hz)	6.66 (1H, d, $J = 16.0$ Hz)
γ	7.64 (1H, d, $J = 16.5$ Hz)	7.63 (1H, d, $J = 16.0$ Hz)	7.92 (1H, d, $J = 16.0$ Hz)	7.96 (1H, d, $J = 16.0$ Hz)
Cinn(R_4)				
2,6	7.54 (2H, d, $J = 8.5$ Hz)	7.54 (2H, d, $J = 9.0$ Hz)	7.65 (2H, d, $J = 7.5$ Hz)	7.67 (2H, d, $J = 8.5$ Hz)
3,5	7.13 (2H, d, $J = 8.5$ Hz)	7.13 (2H, d, $J = 8.5$ Hz)	7.21 (2H, d, $J = 7.5$ Hz)	7.22 (2H, d, $J = 8.5$ Hz)
β	6.32 (1H, d, $J = 15.5$ Hz)	6.30 (1H, d, $J = 16.0$ Hz)	6.45 (1H, d, $J = 16.0$ Hz)	6.47 (1H, d, $J = 16.0$ Hz)
γ	7.60 (1H, d, $J = 15.5$ Hz)	7.59 (1H, d, $J = 16.0$ Hz)	7.82 (1H, d, $J = 16.0$ Hz)	7.84 (1H, d, $J = 16.0$ Hz)

[a] Compounds **1** and **2** were measured in MeOH, while compounds **3** and **4** were measured in C_5D_5N, and the signal assignments of **3** and **4** were aided by COSY, HMQC and HMBC spectra.

TABLE II ^{13}C NMR data of compounds **1**–**4** (125 MHz)[a]

		1	*2*	*3*	*4*	*Tenuifoliose L* [4]
Glc-1	1	93.5	92.7	91.9	91.8	92.7
	2	81.9	81.3	81.4	81.1	81.3
	3	80.0	79.3	78.4	78.3	79.3
	4	70.8	70.5	69.7	69.8	70.5
	5	72.9	69.6	69.0	68.8	69.6
	6	62.6	64.3	63.5	63.3	64.3
Glc-2	1	105.9	105.4	105.6	106.2	105.3
	2	75.3	75.3	75.4	75.4	75.8
	3	79.0	78.5	78.3	78.9	78.5
	4	72.1	71.5	71.3	71.6	71.5
	5	78.3	77.7	77.9	78.0	77.7
	6	63.6	63.1	63.0	63.0	63.1
Glc-3	1	104.7	104.1	104.2	103.8	104.1
	2	75.9	75.4	74.1	73.3	75.4
	3	83.9	83.4	88.0	84.1	83.4
	4	70.1	69.6	69.0	69.1	69.6
	5	72.9	72.4	73.9	71.8	72.4
	6	63.6	63.1	63.6	63.0	63.1
Glc-4	1	105.9	105.4	105.4	105.7	105.3
	2	76.3	75.8	75.4	76.0	75.7
	3	78.9	78.4	77.9	78.0	78.4
	4	72.1	71.5	71.3	71.3	71.5
	5	78.4	77.9	78.4	78.0	77.9
	6	63.4	62.8	62.2	62.4	62.8
Fru	1	66.8	66.3	64.9	65.1	66.3
	2	104.2	103.7	103.5	103.4	103.7
	3	80.9	80.4	79.6	79.8	80.4
	4	74.2	74.0	73.9	73.3	74.0
	5	85.1	84.7	84.8	84.9	84.7
	6	63.8	63.9	63.3	62.6	63.9
Rham	1	99.5	99.6			100.1
	2	72.4	71.9			71.8
	3	72.7	72.2			72.1
	4	74.1	73.7			73.7
	5	71.4	70.9			70.9
	6	18.6	18.1			18.1
Ac(R5)	1		172.5	170.7	170.7	172.5
	2		20.8	20.7	20.8	20.8
Ac(R6)	1	172.5	172.0		170.1	172.0
	2	21.6	21.1		20.9	21.1
Ac(R7)	1	172.7	172.2	170.7	170.6	172.2
	2	20.9	20.4	20.4	20.4	20.4
Bz(R3)	1	131.5	131.0	130.3	130.3	131.0
	2,6	131.6	131.0	130.3	130.3	131.0
	3,5	130.5	130.0	129.0	129.1	130.0
	4	135.4	134.9	133.8	133.8	134.9
	α	167.7	167.1	166.3	166.3	167.1
Cinn(R2)	1	127.6	127.1	125.9	125.8	127.1
	2,6	131.8	131.2	130.7	130.8	131.2
	3,5	117.5	116.9	116.6	116.9	116.9
	4	161.9	161.4	161.5	161.7	161.3
	α	168.9	168.4	166.8	166.8	168.3
	β	115.4	114.9	114.6	114.6	114.9
	γ	147.4	146.9	145.8	145.6	146.9
Cinn(R4)	1	130.1	129.6	125.8	125.8	129.5
	2,6	131.7	131.1	130.7	130.8	131.1
	3,5	118.4	117.9	116.8	116.7	117.9
	4	160.2	159.7	161.6	161.5	159.7
	α	168.2	167.5	166.6	166.5	167.5
	β	117.4	116.7	114.5	114.6	116.7
	γ	146.4	146.1	145.6	145.8	146.1

[a] Compounds **1** and **2** were measured in MeOH, while compounds **3** and **4** were measured in C_5D_5N. and the signal assignments of **3** and **4** were aided by COSY, HMQC and HMBC spectra.

Chemical Co., and the column chromatography silica gel (200–300 mesh) was supplied by the Qingdao Marine Chemical Factory.

Plant Material

The cortexes of *P. tenuifolia* were collected from Shanxi Province, in October 2000. The plant was identified by one of the authors (P.F. Tu). A voucher specimen (No. 001020) is deposited in the herbarium of School of Pharmaceutical Sciences, Peking University, Beijing, China.

Extraction and Isolation

The air-dried roots of *P. tenuifolia* (11 kg) were ground and refluxed three times with 95% EtOH (77 L). The 95% EtOH solution was then combined and evaporated *in vacuo* to yield 4.9 kg of residue, a portion (2 kg) of which was suspended in water and extracted successively with light petroleum, $CHCl_3$ and n-BuOH. Parts of the n-BuOH extract (325 g) were subjected to a macroporous resin D101 column (11.5 × 85.5 cm). The adsorbed material was eluted with H_2O, 20, 50, 70, and 95% EtOH, respectively. The 50% EtOH eluate (78 g) was chromatographed on silica gel (1.6 kg), eluting with $CHCl_3$—MeOH—H_2O in a gradient manner (500 : 1 : 0 → 60 : 40 : 5). Fractions 79–95 (4 g) was first subjected to ODS column chromatography, then purified by HPLC with MeOH—H_2O (50:50) as mobile phase to furnish **3** (45.6 mg) and **4** (139.2 mg). Fractions 96—114 (3 g) were also first subjected to ODS column chromatography, MeOH—H_2O (20 : 80 → 80 : 20) as the eluting solvent, to give 20 fractions; fractions 9–10 were then further subjected to Sephadex LH-20 and finally purified by HPLC, with MeOH—H_2O (50:50) as mobile phase to furnish **2** (72.1 mg). Fractions 133–149 (3 g) were first subjected to ODS column chromatography, then purified by HPLC with MeOH—H_2O (45:55) as mobile phase to furnish **1** (46.9 mg).

Tenuifoliose Q (**1**), white amorphous $[\alpha]_D^{24}$ powder, −92.8 ($c = 0.85$, MeOH). IR ν_{max}^{KBr} (cm^{-1}): 3405 (OH), 1720 (C═O), 1633 (C═C), 1604, 1513, 1452 (aromatic ring). TOF-MS (CCA as matrix) *m/z*: 1477 $[M + Na]^+$. ^1H NMR data: Table I. ^{13}C NMR data: Table II.

Tenuifoliose L (**2**), white amorphous powder, $[\alpha]_D^{24}$ −46.4 ($c = 0.85$, MeOH). TOF-MS (CCA as matrix) *m/z*: 1519 $[M + Na]^+$. ^1H NMR data: Table I. ^{13}C NMR data: Table II.

Tenuifoliose I (**3**), white amorphous powder, $[\alpha]_D^{24}$ −10.7 ($c = 0.89$, MeOH). ESI-MS *m/z*: 1369 $[M + 18]^+$. ^1H NMR data: Table I. ^{13}C NMR data: Table II.

Tenuifoliose H (**4**), white amorphous powder, $[\alpha]_D^{24}$ −60.2 ($c = 0.82$, MeOH). ESI-MS *m/z*: 1327$[M + 18]^+$. ^1H NMR data: Table I. ^{13}C NMR data: Table II.

Acknowledgements

We thank the staff of the NMR measurement center of our University, for measuring the NMR spectra, and the members of MS measurement center of the Chemical Institute, Chinese Academy of Science for providing the MS data.

References

[1] Miyase, T., Iwata, Y. and Ueno, A. (1992), *Chem. Pharm. Bull.* **40**, 2741–2748.
[2] Zhang, D.M., Miyase, T., Kuroyanagi, M., Umehara, K. and Noguchi, H. (1998), *Phytochemistry* **47**, 45–52.
[3] Saitoh, H., Miyase, T., Ueno, A., Atarashi, K. and Saiki, Y. (1994), *Chem. Pharm. Bull.* **42**, 641–645.
[4] Saitoh, H., Miyase, T., Ueno, A. and Atarashi, K. (1993), *Chem. Pharm. Bull.* **41**, 2125–2128.
[5] Jiangshu New Medicinal College (1997), *Dictionary of Chinese Drugs* (Shanghai Scientific Technologic Publisher, Shanghai), p. 2174.